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First-Principles Lattice Dynamics Calculations of the Phase Boundary Between β-Si_3N_4 and γ-Si_3N_4 at Elevated Temperatures and Pressures

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The phase boundary between β-Si_3N_4 and γ-Si_3N_4 is investigated at high pressure and high temperature using first-principles lattice dynamics calculations within the quasi-harmonic approximation. We find a positive slope of the phase boundary. It turns out that the thermal expansion of the spinel-type γ-phase is larger than that of the phenacite-type β-phase. On the other side, pressure affects more the volume of β-Si_3N_4 than of γ-Si_3N_4, reflected in the higher bulk modulus of γ-Si_3N_4. The origin of the different temperature behaviour of these phases, consequently, goes along with a larger volume dependence of the zero point energy in γ-Si_3N_4 in comparison to β-Si_3N_4.

1 Introduction

Almost a decade ago cubic γ-Si_3N_4 with spinel-type structure was realized by high-temperature/high-pressure chemical synthesis[1]. The first report gave a pressure of 15 GPa and a temperature of 2000 K needed to favour the formation of the γ-phase over the β-phase. Computations that went along with the experimental realization indicated a transition pressure of 12.1 GPa. Subsequent experimental studies, which used amorphous silicon and nitrogen containing precursors to exclude kinetic effects of the β-γ transition, located the phase boundary between 10 and 13 GPa at temperatures between 1600 and 2000 K[2]. No account for a direct conversion from the γ-phase to the β-phase has been given, though.

At high temperatures and pressures, it is usually extremely difficult to determine correctly the phase boundaries of solids because large hysteresis effects due to sluggish kinetics are usually present. In this study, we compute the pressure-temperature phase diagram between β- and γ-Si_3N_4 assuming ideal crystals using first-principles lattice dynamics calculations. The crystal structures of β- and γ-Si_3N_4 are shown in Figures 1 and 2, respectively. Si atoms in the phenacite-type β-structure are four-fold approximately tetrahedrally coordinated. In the spinel-type γ-structure two thirds of the Si atoms are octahedrally coordinated, the remaining Si are tetrahedrally coordinated.

2 Methods

All first-principles calculation were carried out with the Vienna *Ab initio* Simulation Package (VASP)[3–5]. We used the projector augmented wave (PAW) method[6] in the framework of density functional theory within the generalized gradient approximation according to

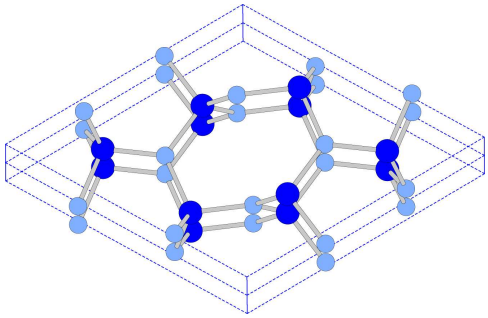

Figure 1. Crystal structure of β-Si_3N_4 ($P6_3/m$). The blue and sky-blue circles denote silicon and nitrogen atoms.

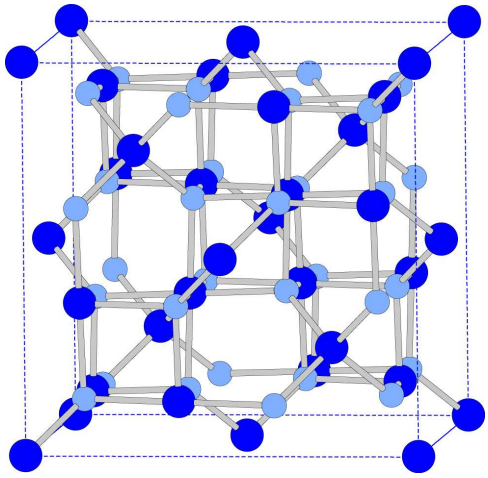

Figure 2. Crystal structure of γ-Si_3N_4 ($Fd\bar{3}m$). The blue and sky-blue circles denote silicon and nitrogen atoms.

Perdew-Burke-Ernzerhof (PBE)[7] together with a cutoff energy of 500 eV for the expansion of the wave function into a plane wave basis set. The phonon contribution to the free enthalpy was calculated using the frozen phonon method as implemented in the *fropho* code[8]. We employed the quasi harmonic approximation (QHA) (e.g.[9]). The free enthalpy like function G(p,T) is computed according to

$$G[p,\,T] = \min_{V} U(V) + F_{\mathrm{phonon}}(V;\;\;T) + pV, \tag{1}$$

When the investigated phase is a stable phase, then G(p,T) corresponds to its free enthalpy.

Here p, T, and V denote pressure, temperature, and volume, respectively. U is the internal energy, and F_{phonon} is the phonon free energy. We computed the bracketed term at selected volume points. Finally, Murnaghan's equation of state[10] was used to fit the calculated values and to derive a bulk modulus.

To allow for an accurate assessment of the free energy, some heavy convergence crite-

ria have to be employed to avoid the appearance of negative frequencies within the Brillouin zone. Energy was converged until the energy differences in consecutive steps were lower than 10^{-9} eV, and force and stress were converged until they became less than 10^{-6} eV, and 10^{-4} GPa, respectively. The Brillouin zones were sampled by a 448 (β-Si_3N_4) and by a 4x4x4 of (γ-Si_3N_4, primitive unit cell) k-point mesh generated according to the Monkhorst-Pack scheme. In the frozen phonon calculations, a finite atomic displacement of 0.01 Å was used. The supercells were built with 2x2x2 unit cells for β-Si_3N_4 and 2x2x2 primitive cells for γ-Si_3N_4. The meshes for the Brillouin zones were sampled to 8x8x20 and 12x12x12 for β-Si_3N_4 and γ-Si_3N_4, respectively.

3 Results and Discussion

In Figure 3 we show the calculated pressure-temperature (P-T) phase diagram of silicon nitride including the two phases β-Si_3N_4 and γ-Si_3N_4. The difference in the free enthalpy like functions between the two phases, hence the value of ΔG, is represented by the intensity of the colour. The phase boundary corresponds to the line drawn; here the difference in ΔG=0. Accordingly, while β-Si_3N_4 is stable at low pressure and γ-Si_3N_4 at high pressure, the slope of the phase boundary between the two phases is found to be positive. Consequently, higher temperatures will require some higher pressures for inducing the β to γ phase transition.

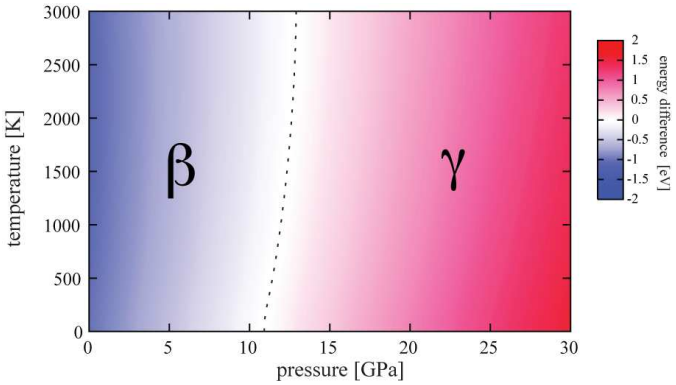

Figure 3. P-T phase diagram. The energies are given per formula unit.

We show the phonon density of states (phonon-DOS) as a function of phonon frequencies of both phases in Figure 4. The phonon-DOS of β-Si_3N_4 is split into two regions. The occurrence of a gap is attributed to the anisotropic crystal structure. Although N is twice as light as Si, nitrogen contributes significantly to the phonon-DOS even in the low-frequency regime. This is due to vibrations in the a-b plane localized at approximately the Brillouin zone boundary. For γ-Si_3N_4 on the other side we don't observe a gap, although a separation into N-dominated high-frequency vibrations and Si-dominated low-frequency vibrations is visible. The compact structure, therefore, drives both regions to overlap considerably.

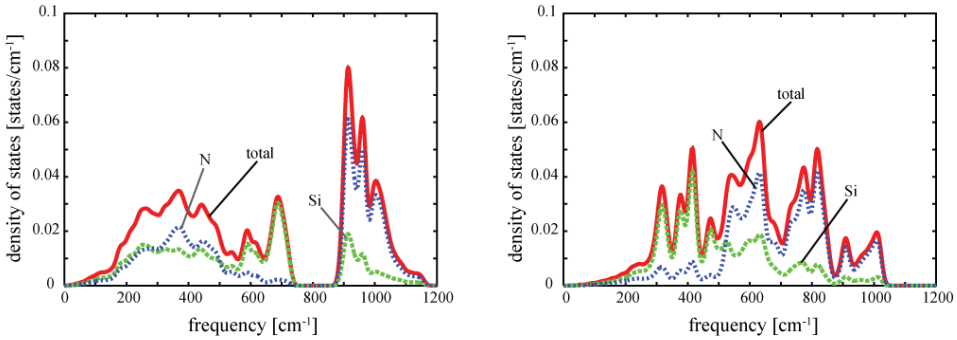

Figure 4. Phonon DOS's of the β-phase (left) and the γ-phase (right).

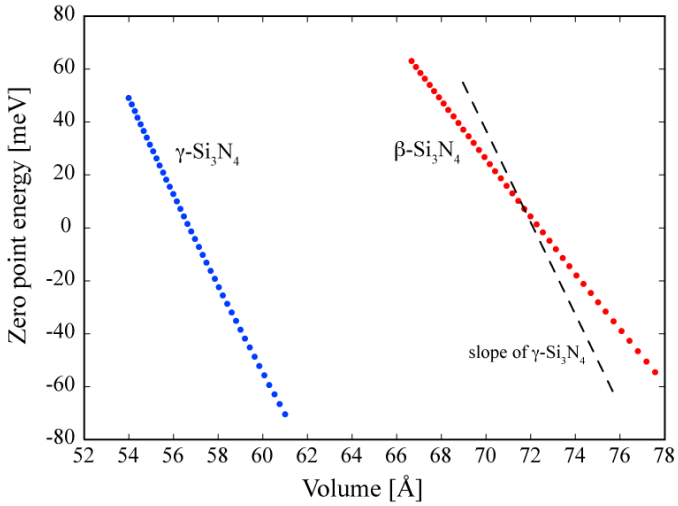

Figure 5. Zero point energies of the β-phase (red points) and the γ-phase (blue points) as a function of volume. To compare their slopes, a copy of γ-phase is placed near that of β-phase. The energies are given per formula unit.

To study the thermal expansion of a solid structure, the volume dependence of its phonon-DOS is a necessary ingredient, since volume and temperature are implicitly related within the QHA. In principle, the phonon free energy also depends directly on temperature. However, in order to investigate the volume dependence of the phonon-DOS only it is usually enough to derive a trend of the phonon free energy with temperature and volume. Therefore, the zero point energy of a phonon system is indicative of how its phonon-DOS changes with volume, because the zero point energy E_{zero} is related to the phonon-DOS via

$$E_{\mathrm{zero}} = \frac{1}{2} \sum_{\mathbf{k},\nu} \hbar\omega(\mathbf{k}, \nu) \tag{2}$$

Here, **k** is a wave vector, and ν a phonon frequency. In Figure 5 we plot the frequency depending part of the zero point energies of β-Si_3N_4 and γ-Si_3N_4 as a function of volume. A negative slope indicates that a volume increase decreases the phonon free energy at 0 K, which is generally expected to be true at finite temperature. However, the data also shows a steeper slope for the curve of γ-Si_3N_4 than for β-Si_3N_4. Consequently, the γ-phase will tend to exhibit a larger thermal expansion than the β-phase.

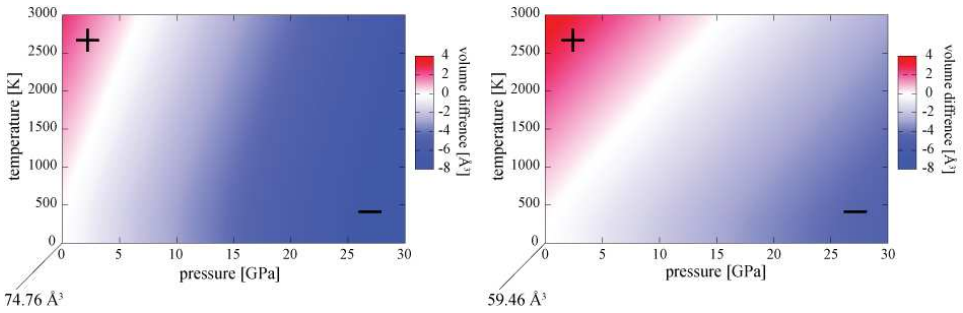

Figure 6. Volume changes of β-Si_3N_4 (left) and γ-Si_3N_4 (right) in the pressure-temperature phase diagram. The change (per formula unit) is indicated relative to their volumes at 0 K and 0 GPa.

The computed volumes of the enthalpy confirm this trend, derived through inspection of the zero point energies. Note, that the enthalpy in turn was assessed as the minimum of computations for several volumes. In Figure 6 we show the overall volume changes of both the β- and the γ-phase in the pressure-temperature space. The thermal expansion of γ-Si_3N_4 is indeed larger than that of β-Si_3N_4. However, at the same time, γ-Si_3N_4 is also less compressible than β-Si_3N_4.

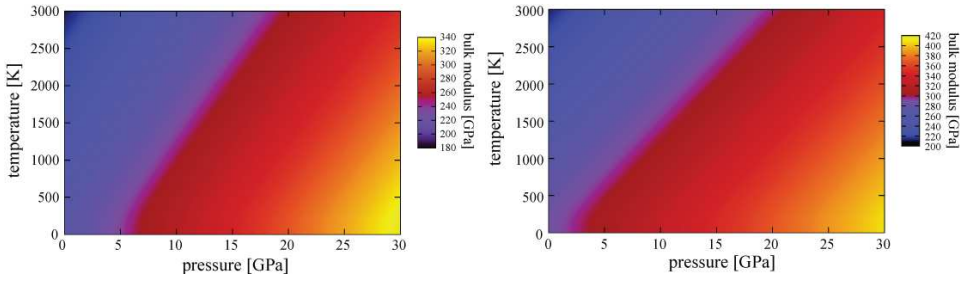

Figure 7. Bulk modulus of β-Si_3N_4 (left) and γ-Si_3N_4 (right) as a function of temperature and pressure.

We present the temperature and pressure dependent bulk modulus, the inverse of compressibility, for β-Si_3N_4 and γ-Si_3N_4 in Figure 7. As is well known, γ-Si_3N_4 has a larger

bulk modulus than β-Si_3N_4. As it turns out, however, temperature affects the bulk modulus of γ-Si_3N_4 more than that of β-Si_3N_4.

4 Conclusions

Using first-principles lattice dynamics calculations to investigate the vibronic contributions to the free enthalpies of phenacite- and spinel-type silicon nitride, we find a positive slope of the phase boundary between β-Si_3N_4 and γ-Si_3N_4 in the pressure-temperature phase diagram. While the spinel-phase has a larger bulk modulus than the phenacite-phase, its thermal expansion is also larger. The reason for this behaviour is the larger volume dependence of the zero point energy in γ-Si_3N_4 in comparison to β-Si_3N_4. Overall, the work of pressure, p·V, dominates the transition pressure of the β to γ transition. The precise slope of the phase boundary, however, is governed by small energy differences, which depend on the explicit phonon structure.

Acknowledgments

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